

# Electronic Structure of Divalent Hexaborides

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## INTRODUCTION

Great interest in the divalent hexaborides has been generated recently by the discovery of high Curie temperature weak-moment ferromagnetism (FM) in La-doped  $\text{CaB}_6$  [1] and by exotic theoretical models to explain the unusual magnetism, *e.g.* that it represents the ground state of a dilute electron gas [2] or of a doped excitonic insulator [3]. The starting point of most thinking about the divalent hexaborides, and central to the excitonic instability model, is the presumed existence of a band overlap between the top of the boron valence states and the bottom of the cation *d*-conduction band at the X-point of the simple cubic Brillouin zone appropriate to these materials. Without such overlap stoichiometric divalent hexaborides would be insulators. Band overlap is predicted by band structure calculations [4] and magneto-oscillatory studies [5] have been interpreted in this semi-metal framework. However, a new quasiparticle band calculation that includes a GW self-energy correction predicts  $\text{CaB}_6$  to have an X-point bandgap of 0.8 eV [6].

Our early angle-resolved photoemission spectroscopy (ARPES) studies at the SRC synchrotron of  $\text{EuB}_6$  and  $\text{SrB}_6$  showed, contrary to the band-overlap picture, an isolated X-point electron pocket separated from the X-point boron valence band maximum by a gap  $>1$  eV. Motivated by the prior theoretical and experimental evidence for bulk band overlap and by certain surface sensitive aspects of the data, we interpreted the observed gap as a property only of the surface region probed in ARPES. The new quasiparticle band calculation provides a theoretical basis for interpreting the X-point bandgap as a bulk property of divalent hexaborides. Reported here are new ARPES measurements of  $\text{CaB}_6$  and  $\text{EuB}_6$  [7], that provide a more detailed view of the *k*-dependent electronic structure and variations of the surface chemical potential with cation and time.

## EXPERIMENT

Single crystal samples of  $\text{CaB}_6$  and  $\text{EuB}_6$ , grown from an aluminum flux using powders prepared by boro-thermally reducing cation oxides, were cleaved in ultra-high vacuum ( $<4 \times 10^{-11}$  torr) at  $\approx 30\text{K}$  exposing the [001] surface for ARPES measurements at ALS Beamline 10.0.1. The ability to rotate the HERS spectrometer relative to the incident beam polarization allowed for measurement in two different symmetry selection geometries, *i.e.* p- and s-polarization. A total instrumental resolution of  $\approx 40$  meV and full angular acceptance of  $\approx 0.2^\circ$  was employed.

## RESULTS

Figures 1(a,b) show the experimentally measured band structure for  $\text{CaB}_6$  along  $\Gamma$ -X for the two different p- and s-polarization geometries. The data exhibit strong initial state symmetry selection rule effects. Fig. 1(c) shows a sum of the two polarization data sets with comparison to the GW calculated band structure [6]. Identification of all the calculated bands in the summed data, but not for the individual polarizations, highlights the utility and importance of having this rotational capability of the HERS detector. The bands selected by the s-polarization geometry correspond to the theory bands labeled 2 and 5, both of which have the same symmetry label of  $\Delta_5$ .

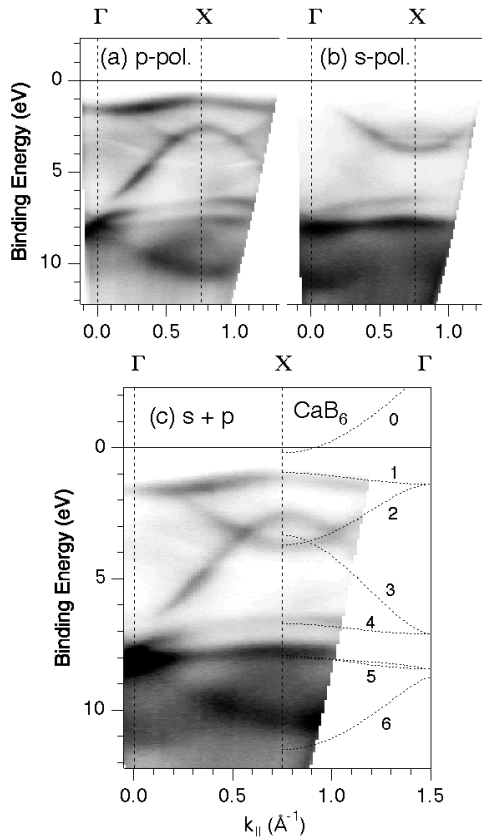


Fig. 1. Comparison of the experimental and theoretical band structures of  $\text{CaB}_6$  along  $\Gamma$ -X. The reverse gray scale image of angle-resolved photoelectron intensities is the sum of two data sets with 30 eV s- and p-polarized excitation. Dashed lines are from the quasiparticle GW calculation [6] shifted by 0.45 eV to lower energy.

The qualitative agreement between experiment and theory dispersions in Fig. 1(c), most importantly including the existence of a band gap near  $E_F$ , is very striking. The theory bands have been rigidly shifted by 0.45 eV to lower energy for better visual alignment to the experimental data. Quantitative discrepancies, however, are also quite visible, including: (i) the size of the band gap near  $E_F$ , (ii) the overlap between bands 2 and 3, (iii) the overall boron-block bandwidth (between bands 1 and 6), and (iv) an additional weak broad dispersion at the bottom of the valence band.

This latter counter-dispersing band, 11 eV at  $\Gamma$  to  $\approx 9$  eV at X is suggestive of band back-folding resulting from a periodicity doubling. Indeed, low energy electron diffraction (LEED) images of freshly cleaved  $\text{CaB}_6$  surfaces exhibit  $2 \times 1$  surface order. The absence of conduction band intensity (band 0) at  $E_F$  for  $\text{CaB}_6$  in Fig. 1 implies a  $>1$  eV band gap and insulating behavior. While this result agrees with electron counting for stoichiometric material, it does not agree with bulk Hall transport measurements of electron carriers and dHvA measurement of Fermi surfaces. Also, as noted, earlier ARPES measurements of  $\text{EuB}_6$  and  $\text{SrB}_6$  both showed X-point electron pockets and ellipsoidal Fermi surface contours, contrary to this  $\text{CaB}_6$  data set.

To address these different results for different cations, we present in Fig. 2 ARPES measurements along  $\Gamma$ -X for  $\text{EuB}_6$  for the p-polarization geometry. Similar to the  $\text{CaB}_6$  data in Fig. 2(a), the  $\Delta_5$  symmetry bands (2 and 5) are absent and no states near  $E_F$  are observed (see top panels of Fig. 2). However, this surface exhibited a very interesting time dependent behavior, illustrated by Fig. 2(b,c), in which the emergence of a small electron pocket at the X-point (corresponding to band 0 in Fig. 1) is observed at  $\approx 4$  hours after cleavage of the sample. Accompanying this change at  $E_F$ , some additional redistribution of spectral weight in the boron block bands also occurs (illustrated by a comparison of X-point spectra in Fig. 2(c)). In addition, while the surface order before and after the spectral changes in this sample is not known, another important difference between  $\text{EuB}_6$  and  $\text{CaB}_6$  is the observation of  $1 \times 1$  versus  $2 \times 1$  LEED, respectively, performed after the ARPES experiments.

While the mechanism for this temporal change is not yet understood, it is important to note that the existence of the  $>1$  eV X-point gap between bands 0 and 1 does *not* change — only the position of the chemical potential varies. Presumably band bending near the surface either relaxes an insulating surface layer or creates a metallic surface two-dimensional electron gas. The former is implied by bulk transport and dHvA measurements which show n-type carriers and the existence

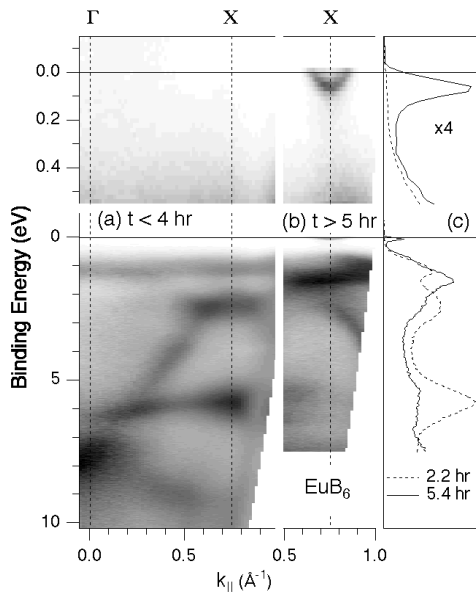


Fig. 2. Time dependent change in the band structure of  $\text{EuB}_6$ , (a)  $t < 4$  hours and (b)  $t > 5$  hours after the initial cleave. The reverse gray scale images are measured with p-polarized 30 eV excitation. (c) Comparison of X-point spectra. Upper panels show an expanded region near  $E_F$ .

of small elliptical Fermi surface pockets for the bulk electronic structure. The ability to simultaneously measure the complete band dispersions at the X-point using the angular mode of the Scienta analyzers was crucial to the discovery and monitoring of such time-dependent changes. Complementary bulk-sensitive soft x-ray absorption and emission measurements at the boron K-edge performed at ALS Beamline 8.0 [8] also provide an (angle-integrated) confirmation of the existence of a bulk band gap consistent with the ARPES data.

In summary, the existence of a semiconducting bandgap (rather than a semimetallic band overlap) is observed in the divalent hexaborides, thereby ruling out the excitonic insulator model for the novel FM in La-doped  $\text{CaB}_6$ . The location of the chemical potential at the bottom of conduction band indicates non-stoichiometric defects contributing excess electrons. The likely defects are boron vacancies, recently shown to carry magnet moments [9], and may be relevant to the novel ferromagnetism discovered in doped and undoped divalent hexaborides.

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